United States Patent Office

3,256,188

Patented June 14, 1966

1

3,256,188
OIL-SOLUBLE METAL HALIDE COMPLEXES AND IMPROVED LUBRICATING OIL COMPOSITIONS CONTAINING SAME

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No Drawing. Filed June 21, 1963, Ser. No. 289,711
19 Claims. (Cl. 252—42.7)

This invention relates to certain oil-soluble metal halide complexes and to improved lubricating oil compositions containing these complexes.

It is well known that lubricating oils of both the petroleum and synthetic type are subject to oxidative deterioration, particularly under conditions of high temperature and pressure encountered in internal combustion engines. This oxidation produces acidic products in the oil which products are corrosive to the metal parts of the engine.

It is also known in the art that lubricating oils such as refined petroleum oil fractions, are generally not capable of maintaining a lubricating film between engaged metal surfaces where the unit load at the engaged surfaces exceeds a pressure of several thousand pounds per square inch.

In order to overcome, insofar as possible, the deleterious effects of oxidation in lubricating oils and to increase the extreme pressure (E.P.) characteristics of these oils, it has become the practice to add small amounts of antioxidants and E.P. agents thereto.

For the most part, the agents heretofore employed have been organic compounds or metal derivatives thereof. This is due primarily to the greater oil solubility of these organic compounds as compared to that of inorganic compounds.

Inorganic compounds such as metal halides are, in general, insoluble or only slightly soluble in mineral oils. Metal halides can be physically dispersed in mineral oils by using various milling techniques alone or in conjunction with the use of oil-soluble dispersing agents. Such physical dispersions, however, have limited use in lubricating oils due to the fact that they are unstable and the dispersed phase has a tendency to precipitate.

It would, of course, be desirable to completely solubilize these metal halides in the oil compositions. In some cases, this has been accomplished through the use of high molecular weight dispersants such as metallic sulfonates. However, such high molecular weight materials generally tend to interfere with the action of the metal halides to such an extent that the desirable additive characteristics of these salts are lost.

Accordingly, it is an object of the present invention to provide certain metal halides complexes capable of imparting both superior anti-oxidant and good E.P. characteristics to lubricating oils, which halide complexes are substantially completely oil-soluble and therefore do not exhibit a tendency to precipitate from mineral oil compositions.

A further object is to provide metal halide complexes which because of their oil-solubility do not require the use of extraneous dispersing agents which tend to interfere with the desirable additive characteristics of the metal halides.

Another object of the invention is to provide a simple and effective process for producing oil-soluble metal halide complexes.

A further object is to provide improved lubricating oil compositions containing these metal halide complexes and possessing good oxidation stability and extreme pressure characteristics.

Other objects of this invention and some additional advantages thereof will become apparent hereinafter.

2

According to the present invention we have found that metal halides complexes capable of imparting both good anti-oxidant and improved E.P. characteristics to lubricating oils and which are substantially completely soluble in oil, can be obtained by complexing certain metal halides with selected alcohols.

The formation of these oil-soluble complexes is carried out by contacting the metal halide with an amount of the alcohol sufficient to effect the solubilization thereof. Temperatures such as room temperature or elevated temperatures below the boiling point of the alcohol may be used. Mild heating to a temperature such as 100° C. often helps to speed up the solubilization process. The complex is generally obtained in the form of a clear solution. If desired, the resulting solution may be filtered or otherwise purified to remove any undissolved materials which may be present.

Although this invention is not limited to any particular theory, it is believed that the metal halides and alcohols form metal halide-alcohol complexes of presently undetermined structure. The complexes, which are in the form of clear solutions, possess good solubility in both petroleum and synthetic lubricating oils, in contrast to the metal halides per se which are generally oil-insoluble. In addition, these metal halide complexes are capable of imparting both good oxidation stability and improved E.P. characteristics to the lubricating oils.

The oil-soluble complexes of this invention may, in general, be prepared from any metal chloride, metal bromide or metal iodide which is solubilized by and complexes with the particular alcohol complexing agents. Some preferred examples of suitable halides of this type include the chlorides, iodides and bromides of metals from Groups I to IV, VI and VIII of the Mendeléeff Periodic Table. The chlorides, bromides and iodides of metals such as potassium, zinc, cadmium, aluminum, tin, chromium, iron and cobalt are particularly preferred.

The alcohols which form the complexes with the metal halides according to the present invention are saturated or olefinically unsaturated, straight chain or branched chain, aliphatic alcohols containing from 5 to about 20 carbon atoms. Either a single alcohol or mixtures of at least two alcohols may be used.

Some examples of suitable alcohols include 2-ethyl hexanol, n-octanol, tridecanol, and mixtures of alcohols from about 8 to about 10 carbon atoms produced by the oxo process from olefinic hydrocarbons.

The relative proportions of the metal halide and the alcohol used in the preparation of the complex depends largely on the solubility of the particular halide. In general, an amount of alcohol at least sufficient to solubilize the metal halide is employed, although, of course, a large excess of alcohol may be used if desired.

The amount of metal halide present in the complex also depends primarily on the solubility of the halide. Metal halide-alcohol complexes containing from about 1.0 to 25.0 percent by weight of metal halide are preferred.

The oil soluble metal halide-alcohol complexes of this invention are capable of improving the oxidation stability and E.P. characteristics of a wide variety of petroleum base and synthetic, e.g., synthetic hydrocarbon and synthetic ester, lubricating oils.

The petroleum lubricating oils would include mineral oils from a variety of different crude stocks, both solvent and acid refined, hydrocracked, etc. Some examples of synthetic hydrocarbon oils include hydrogenated polyolefins, alkyl benzene, etc. Synthetic esters would include di-2-ethylhexyl sebacate, di-octyl adipate, trimethylol propane trioctanoate, pentaerythritol tetraheptanoate, etc.

The amount of the metal halide-alcohol complex used in the lubricating oil will depend on various factors such as the particular nature of the oil, the intended use thereof, etc.

In general from about 0.1% to about 25% by weight, preferably from about 1.0% to about 10% should be employed.

The following examples are given in order to further illustrate the present invention without in any way limiting its scope.

EXAMPLE 1

Twenty grams of $SnCl_4 \cdot 5H_2O$ were stirred in 80 grams of n-octanol at room temperature until all the salt dissolved. The resulting clear, colorless solution had good oil solubility in both mineral and ester lubricating oils. Upon analysis the product was shown to contain 9.3% chlorine and 6.5% tin.

EXAMPLES 2–11

Following the procedure of Example 1, additional oil-soluble, metal halide-alcohol complexes were prepared as reported in the following Table 1.

The complexes were then admixed with an acid treated, clear paraffinic oil supplied under the name "Nujol," to form oil solutions containing about 5% of the complex. The solutions were allowed to stand at room temperature for 30 days, and at the end of this period their clarity was noted.

Table 1

Ex. No.	Metal Halide	Alcohol	Metal, Percent	Halogen, Percent	Color of Solution	Oil Solution [1] After 30 Days at Room Temp.
1	$SnCl_4 \cdot 5H_2O$	n-Octanol	6.5	9.3	Colorless	Clear.
2	$FeCl_3 \cdot 6H_2O$	2-ethyl hexanol	1.8	3.7	Orange	Do.
3	$CrCl_3$	n-Octanol	4.7	8.2	Violet	Do.
4	$FeCl_3$	do	3.5	6.7	Orange	Do.
5	$SnCl_4$	do	11.4	13.2	Colorless	Do.
6	$CoCl_2$	do	4.3	5.3	Blue	Do.
7	$ZnBr_2$	do	5.3	8.9	Colorless	Do.
8	CdI_2	do	3.0	6.1	do	Do.
9	$ZnBr_2$	Tridecanol	2.9	6.6	do	Do.
10	ZnI_2	n-Octanol	3.4	11.4	do	Do.
11	$CoBr_2$	do	2.1	6.1	Blue	Do.

[1] A 5% solution of the complex in an acid refined, clear paraffinic oil supplied under the name "Nujol".

It will be noted from the data of Table 1 that in each case, the complexes were obtained in the form of oil-soluble, clear solutions which retained their clarity even after standing at room temperature for one month.

CATALYTIC OXIDATION TEST

In order to demonstrate the anti-oxidant characteristics of the metal halide-alcohol complexes, lubricating oil compositions containing the complexes of the working examples were subjected to a catalytic oxidation test. Oil compositions containing well-known, commercial anti-oxidants such as zinc dialkyl dithiophosphates were also tested. This test is a recognized one to determine the effectiveness of an additive in preventing the catalytic oxidation of an oil.

The test procedure is as follows. In a 200 by 25 mm. test tube there is placed a 25 cc. sample of the test oil having immersed therein, (a) 15.6 square inches of sand-blasted iron wire, (b) 0.78 square inch of polished copper wire, (c) 0.87 square inch of polished aluminum wire, and (d) 0.167 square inch of a polished lead specimen. This oil is heated to a temperature of 325° F. and maintained at this temperature, while dry air is being passed therethrough at a rate of 10 liters per hour for 24 hours.

The milligram atoms of metal in the additive necessary to maintain the neutralization number (milligrams of KOH required to neutralize 1 gram of test oil) of the oil blend at a value of 2.0 is taken as the measure of its anti-oxidant ability. Thus, the smaller amount of metal required to maintain the neutralization number of 2.0, the higher is the anti-oxidant ability of the additive.

The results of this test are given in Table 2.

Table 2.—Catalytic oxidation test

Complex of Example No.	Anti-oxidant Activity [1]	
	(Mg.-atoms of metal)	(Mg. of metal)
3 ($CrCl_3$ Complex)	1.67	0.087
4 ($FeCl_3$ Complex)	1.18	0.066
6 ($CoDl_2$ Complex)	0.95	0.056
7 ($ZnBr_2$ Complex)	0.52	0.034
8 (CdI_2 Complex)	0.75	0.084
10 (ZnI_2 Complex)	0.36	0.023
11 ($CoBr_2$ Complex)	0.27	0.016
Zinc Di(methyl isobutyl carbinol) dithiophosphate	0.42	0.027
Zinc Di(N-octyl) dithiophosphate	1.69	0.110

[1] The oil used was a SAE 20, solvent refined, Penna. Oil.

From the results reported in Table 2, it will be noted that the metal halide-alcohol complexes are comparable and, indeed, slightly superior in their anti-oxidant properties to well known anti-oxidants such as the zinc di(methylisobutylcarbinol) or di(n-octyl) dithiophosphates.

SAE 1000 R.P.M. LOAD TEST

The E.P. characteristics of the metal halide-alcohol complexes were tested in the SAE 1000 r.p.m. test.

This test, which is commonly accepted in the art as a standard, is used to determine the extreme pressure characteristics of lubricants. The test procedure is described in SAE Journal 39, 23–4 (1936). In general, the oil sample to be tested is placed in an SAE machine as lubricant for two steel test rings which are rotated at different speeds against each other in the same direction so as to produce a combination of rolling and sliding action while a gradually increasing load is mechanically applied. The shaft rotates at 1000 r.p.m. and the rubbing ratio is 14.6 to 1. The break-in load is 20 pounds and the load rate increase is 75 pounds per minute. The test is continued until scoring or seizure occurs. The results obtained are given as pounds scale reading at the end of the test and are reported in the following Table 3.

Table 3.—SAE 1000 r.p.m. test

Composition	Additive, percent	Metal Salt, percent	Seizure Load (gauge lbs.)
(1) Base Oil [1] alone			20
(2) Base Oil [1] plus complex of Ex. No. 1	5	1	345, 370
(3) Base Oil [1] plus high performance E.P. additive [3]	10		360
(4) Base Oil [2] alone			20
(5) Base Oil [2] plus complex of Ex. No. 2	10	1	460+, 460+

[1] The base oil used was a SAE 90, solvent refined Mid-Continent Oil.
[2] The base oil used was an acid refined, clear paraffin oil (Nujol).
[3] Commercial E.P. additive for multi-purpose gear oils meeting the requirements of Military Specification ML-21-L-2105B.

It will be seen from Table 3 that the metal halide-alcohol complexes of the invention impart improved load characteristics to the oils and give results comparable to and even superior to a high performance commercial E.P. additive.

The lubricating compositions of this invention may also contain in addition to the metal halide complexes, effective quantities of various other additives normally used in lubricating compositions, such as detergents, V.I. improvers, pour point improvers, etc.

Although the invention has been described with reference to certain preferred embodiments, it should be understood that various modifications and variations may, of course, be practised without departing from the scope and spirit thereof.

Having thus described the invention, what we desire to secure and claim by Letters Patent is:

1. A process for producing oil soluble metal halide complex reaction products comprising the step of reacting a metal halide, selected from the group consisting of metal chlorides, metal bromides, and metal iodides, with a liquid alcohol selected from the group consisting of saturated and olefinically unsaturated aliphatic alcohols, containing from about 5 to about 20 carbon atoms wherein said reaction product contains from about 1% to 25% of metal halide.

2. A process for producing oil soluble metal halide complex reaction products comprising the step of reacting a metal halide, selected from the group consisting of metal chlorides, metal bromides, and metal iodides, with a liquid alcohol selected from the group consisting of 2-ethyl hexanol, normal-octanol, tridecanol and mixtures of alcohols of from about 8 to about 10 carbon atoms, while maintaining the liquid reaction mixture at a temperature in the range of about 20° to 100° C. wherein said reaction product contains from about 1% to 25% of metal halide.

3. The process of claim **1**, wherein the metal halide is zinc bromide.

4. The process of claim **1**, wherein the metal halide is zinc iodide.

5. The process of claim **1**, wherein the metal halide is cobalt bromide.

6. The process of claim **1**, wherein the metal halide is tin chloride.

7. The process of claim **1**, wherein the metal halide is iron chloride.

8. An oil-soluble metal halide-alcohol complex obtained by complexing a metal halide selected from the group consisting of metal chlorides, metal bromides, and metal iodides with at least an amount of alcohol sufficient to dissolve the metal halide therein, said alcohol being selected from at least one member of the group consisting of saturated aliphatic alcohols and olefinically unsaturated aliphatic alcohols containing from 5 to about 20 carbon atoms wherein the said complex contains from about 1% to about 25% by weight of metal halide.

9. The oil-soluble metal halide complex of claim **8**, wherein the metal halide is zinc bromide.

10. The oil-soluble metal halide complex of claim **8**, wherein the metal halide is zinc iodide.

11. The oil-soluble metal halide complex of claim **8**, wherein the metal halide is cobalt bromide.

12. A lubricating oil composition comprising a major proportion of a lubricating oil and a metal halide-alcohol complex, in an amount sufficient to improve the antioxidant and extreme pressure characteristics of the composition, said metal halide-alcohol complex being obtained by complexing a metal halide selected from the group consisting of metal chlorides, metal bromides, and metal iodides with at least an amount of alcohol sufficient to dissolve the metal halide therein, said alcohol being selected from at least one member of the group consisting of saturated aliphatic alcohols and olefinically unsaturated aliphatic alcohols containing from 5 to about 20 carbon atoms.

13. The lubricating composition of claim **12**, wherein the metal halide-alcohol complex is present in an amount from about 0.1 to 25% by weight.

14. The lubricating composition of claim **12**, wherein the metal halide-alcohol complex is present in an amount from about 1.0 to about 10% by weight.

15. The lubricating composition of claim **12**, wherein the metal halide of said metal halide-alcohol complex is zinc bromide.

16. The lubricating composition of claim **12**, wherein the metal halide of said metal halide-alcohol complex is zinc iodide.

17. The lubricating composition of claim **12**, wherein the metal halide of said metal halide-alcohol complex is cobalt bromide.

18. The lubricating composition of claim **12**, wherein the metal halide of said metal halide-alcohol complex is tin chloride.

19. The lubricating composition of claim 12, wherein the metal halide of said metal halide-alcohol complex is iron chloride.

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Disclaimer

3,256,188.—*Andreas G. Papayannopoulos*, Woodbury, and *Herbert Myers*, Cherry Hill, N.J. OIL-SOLUBLE METAL HALIDE COMPLEXES AND IMPROVED LUBRICATING OIL COMPOSITIONS CONTAINING SAME. Patent dated June 14, 1966. Disclaimer filed Nov. 18, 1968, by the assignee, *Mobil Oil Corporation.*

Hereby enters this disclaimer to claims 12, 15 and 16 of said patent.

[*Official Gazette April 8, 1969.*]